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An FT-IR Spectroscopic Study of the Crystalline and Columnar Liquid-Crystalline Phases of Copper (II) Carboxylates

Rui Fausto[1a], M. F. Ramos Moita[b] and Maria Leonor T. S. Duarte[b]

[a]Departamento de Química, Universidade de Coimbra, P–3049 Coimbra (Portugal)
[b]Departamento de Química, Universidade de Lisboa, P–1700 Lisboa (Portugal)

The FT–IR spectra of a series of anhydrous copper (II) carboxylates of general formula $Cu_2[CH_3(CH_2)_nCOO]_4$ (n= 4–8, 10, 12, 14, 16) show notable changes with the phase transition from the crystalline to the columnar liquid–crystalline phase. These changes indicate that the coordination of the carboxylate groups to the bimetallic centre changes from bridging bidentate to chelating bidentate, which in turn. is induced by the conformational disordering in the carbon chains.

1. INTRODUCTION

Besides their practical importance in industry [1,2], carboxylate complexes of copper (II) present very interesting physicochemical properties (*e.g.*, thermotropism [2-4]), which also make them a challenge to fundamental investigation.

The crystal structures of some copper (II) carboxylates at room temperature have been determined by x–ray crystallography [5-7] and it was shown that these compounds exhibit a tetrakis(carboxylate)dimetal (bridging bidentate) coordination in the crystalline lamellar phase, in which planes of polar copper carboxylate groups are separated by a double layer of aliphatic chains [8,9]. Upon heating, copper (II) carboxylates having a carbon chain with at least five carbon atoms exhibit liquid crystalline mesophases [4,8,9]. Above *ca.* 120 °C, a columnar liquid crystalline phase is formed, consisting of columns of carboxylate polar groups surrounded by disordered aliphatic chains forming a two dimensional hexagonal lattice [4,8,9]. Though some important features of the structure of this mesophase had already been analysed previously [8,9-12], its precise characterization at a molecular level had not yet been established. In this study, FT–IR spectroscopy is used to look at the solid→mesophase transition in a series of anhydrous copper (II) carboxylates.

2. EXPERIMENTAL

The compounds ($Cu_2[CH_3(CH_2)_nCOO]_4$; n= 4–8, 10, 12, 14, 16 – abreviated CuC_{n+2}) were synthesised and purified as described elsewhere [13], and its purity was checked by

[1]Author to whom all correspondence should be addressed

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elemental analysis, differential scanning calorimetry and x-ray crystallography. Infrared spectra of the crystals were obtained as KBr pellets on a Perkin Elmer 1760 FT–IR spectrometer, and those of the mesophases were recorded on a Nicolet FT–IR 800 system using a specially designed transmitance high temperature cell with KBr windows. In both cases the spectral resolution was set up as 2 cm^{-1}.

3. RESULTS AND DISCUSSION

The infrared spectra of all studied compounds show very similar profiles within each phase. On the other hand, marked differences are observed upon phase transition, in particular in the 1600–1400 cm^{-1} spectral region (Fig.1), where the bands due to the νCOO stretching modes (symmetric and antisymmetric) occur: *(i)* the band at *ca.* 1585 cm^{-1} (νCOO as. in the crystal) reduces its intensity considerably, *(ii)* a new band also ascribable to νCOO as. is observed at *ca.* 1540 cm^{-1} (in general showing a shoulder at *ca.* 1530 cm^{-1}), thus appearing at a wavenumber which is *ca.* 45-50 cm^{-1} lower than those of the single band ascribed to this vibration in the crystal, *(iii)* the band ascribed to the νCOO s. mode (1425 cm^{-1} in the crystal) splits, giving rise to a pair of overlaped bands at *ca.* 1425 and 1417 cm^{-1}, and *(iv)* the bands observed in the 1450–1400 cm^{-1} region due to the δCH_2 scissoring and δCH_3 antisymmetric bending modes broaden considerably.

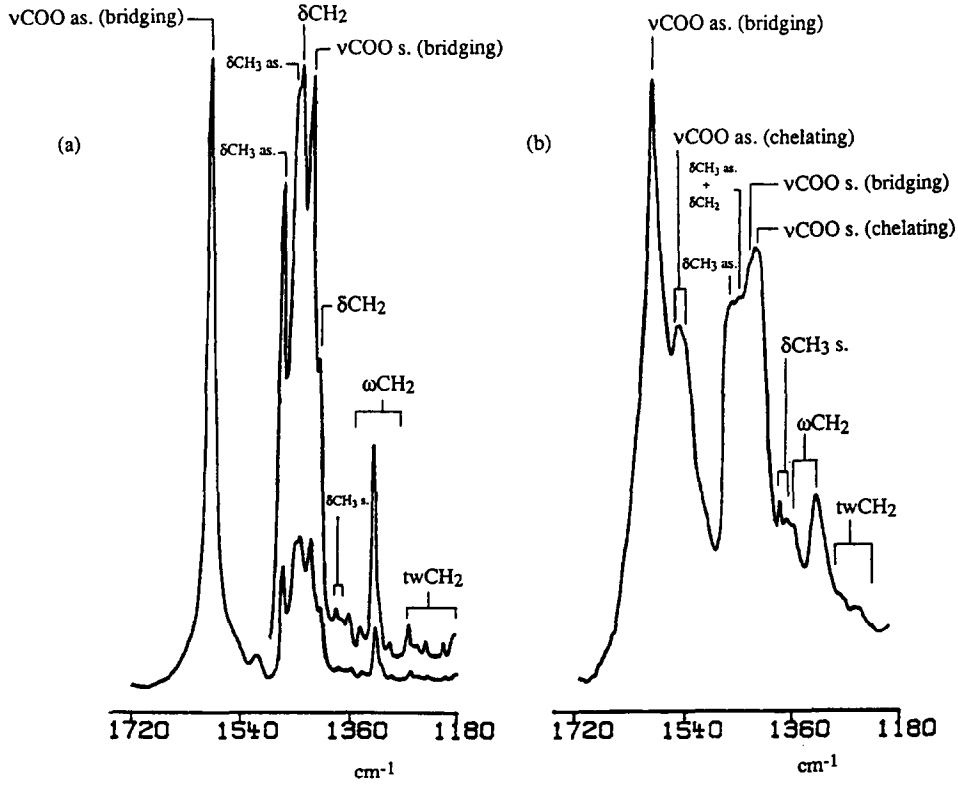
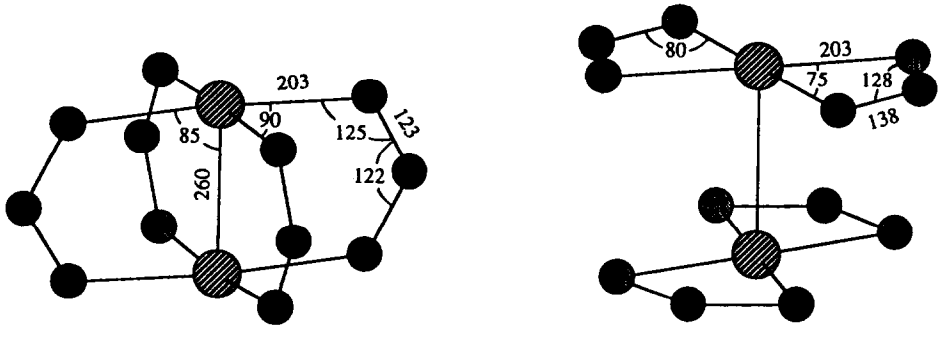


Fig.1- Typical FT-IR spectra profile of the studied copper (II) carboxylates in the 1600-1400 cm^{-1} region, showing relevant band assignments: *a)* crystal (room temperature); *b)* columnar mesophase (*ca.*, 150 °C).

The observed changes both in the intensities and frequencies of the bands due to the νCOO stretching modes with the phase transition – in particular the appearance of new bands –, point to an alteration of the coordination type associated with the mesophase formation. Indeed, though an increase in the carbon cain conformational disorder must necessarily occurs (this explains, for example, the observed broadening of the bands ascribed to the CH bending modes) and this may indirectly provide the driving force leading to the coordination type modification, the observed changes in the νCOO spectral signatures are too much pronounced to be ascribed just to a "second order" effect like this one. Thus, the new νCOO stretching bands near 1540 and 1417 cm^{-1} may be ascribed respectively to the νCOO as. and νCOO s. vibrations of those molecules exhibiting a different type of coordination from the bridging bidentate structure found in the crystals. Considering the $\Delta\nu$COO= νCOO as. - νCOO s values associated with these new bands (*ca.* 120 cm^{-1}) it can be proposed that the new type of coordination should correspond to a chelating bidentate structure (Fig.2), which is also found, for example, in zinc and cadmium long chain carboxylates at room temperature [14]. It must be noted that the FT-IR results clearly demonstrate that in the mesophase there is a simultaneous presence of the two types of coordinating structures (bridging and chelating), as besides the new νCOO bands due to the chelating carboxylates, the νCOO bands assigned to bridging carboxylates also appear in the spectra of the mesophase at frequencies similar to those found in the crystal. From the temperature dependence of the relative intensities of the 1540 and 1585 cm^{-1} bands, and assuming that in the mesophase an equilibrium exists between the two types of coordination, the results point to a bridging structure having an higher energy in this phase than the chelating coordination, as might be expected. Since the I_{1540}/I_{1585} intensity ratio increases with the carbon chain length, the energy difference between the two types of coordination is larger for the higher members of the series of molecules studied. Thus, these results reinforce our conclusion that carbon chain conformational disordering plays a very important role in determining the structural changes, including the change in the coordination type, occurring at the phase transition.



bridging bidentate coordination

chelating bidentate coordination

Fig.2 – Carboxylate–metal coordination structures of copper (II) carboxylates in the crystalline (bridging bidentate coordination) and columnar liquid–crystalline (chelating bidentate coordination). The indicated geometric parameters (in units of pm or degrees) for the crystal were typical values taken from available x–ray or EXAFS data [5-7,10]; those presented for the mesophase were obtained by molecular modelling in this study.

The proposed arrangement of the chelating bidentate carboxylates around the copper atoms (see Fig.2) occurring in the mesophase is consistent with the data previously obtained by EXAFS [10], which enabled to conclude that, though a structural modification around the binuclear copper core at the phase transition occurs, the number of oxygen atoms around each copper atom are the same, the Cu–O bond lengths do not change appreciably, and only a very slight increase in the Cu–Cu bond length seems to occur, the main structural changes involving angular distortions. Indeed, besides being geometrically possible, the bridging bidentate→ chelating bidentate modification is also possible in mechanistic terms, since it may occur by means of a $\approx 90°$ concerted rotation of the four carboxylate groups, implying only minor changes in both the O–C–O and O–Cu–O angles (which have to increase and decrease a bit, respectively) and a small lengthening of the C–O bonds (see Fig. 2).

Note that the required lengthening of the C–O bonds agrees with the observed frequency red shift found for the νCOO stretching modes (in particular for νCOO as.) which gives rise to new bands. In turn, the slight lengthening of the Cu–Cu distance observed by EXAFS upon phase transition [10] is also consistent with the proposed change in the type of coordination, as the presence of the bridging carboxylates in the crystal certainly tends to force the copper atoms to aproach to each other.

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